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## DIFFUSION MASS EXCHANGE IN DISSOLVING SILICA IN Na<sub>2</sub>O – SiO<sub>2</sub> MELTS

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Based on experimental materials on the kinetics of dissolution of silica grains accumulated in the literature, a generalized dependence is obtained, according to which kinetic dissolution curves in diffusion mass exchange are uniquely determined by the chemical composition (silica modulus), the melting temperature, and the initial granulometric composition of silica-bearing batch components.

The process of dissolving silica in silicate melts is a typical heterogeneous reaction with diffusion kinetics.

According to an arbitrary scheme reflecting the mechanism of this process, the most active Na<sup>+</sup> ions diffuse from the melt to the grain surface, where the chemical reaction of silicate formation takes place. The discharge of reaction products containing silicon dioxide in the bonded form proceeds by means of diffusion mass exchange between the silicate layers with different SiO<sub>2</sub> concentrations forming around the grain and the rest of the molten glass.

The scientific literature has accumulated an extensive experimental database on the kinetics of dissolution of silica in silicate melts [1–4]. Analysis of available information has demonstrated that the kinetics of the glass formation process in the conditions of diffusion mass exchange typical of practical glass melting can be generally represented by a functional dependence on the following parameters: the chemical composition of glass, the melting temperature, and the granulometric composition of silica-bearing batch components.

By selecting empirical formulas with subsequent verification of their suitability and adequacy to experimental data it was found that the following power dependence is the most adequate for describing the kinetics of dissolution of silica grains:

$$m = K \tau^n,$$

where  $m = \frac{G_0 - G}{G_0}$  is the part of dissolved SiO<sub>2</sub> ( $G_0$  is the initial quantity of SiO<sub>2</sub>;  $G$  is the quantity of SiO<sub>2</sub> that has not reacted);  $K$  is the numerical coefficient;  $\tau$  is the melting time;  $n$  is the power depending on the melting temperature and the initial size of particles, i.e., on the initial reaction surface area.

Tables 1 and 2 show the results of mathematical processing of experimental data [1, 2] obtained in studying the effect of melting temperature and initial size of sand grains on the rate of batch melting. These studies considered samples melted in a silit furnace from batch with silica modulus

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TABLE 1

Melting temperature, °C	Share of SiO <sub>2</sub> that has reacted, * %, for melting duration, sec								Kinetic dependence $m = K \tau^n$
	600	1200	1800	2400	3000	3600	4800	6000	
1100	—	0.7902	—	0.8619	—	0.8918	0.9327	0.9449	$m = 0.5460\tau^{0.0588}$
1150	—	0.8670	—	0.9257	—	0.9483	0.9680	0.9774	$m = 0.6365\tau^{0.0474}$
1200	0.8236	0.9252	0.9349	—	0.9718	—	0.9910	—	$m = 0.7381\tau^{0.0328}$
1250	0.8998	0.9444	0.9715	—	0.9738	—	0.9797	—	$m = 0.8077\tau^{0.0232}$
1300	0.9573	0.9742	0.9787	—	0.9884	—	—	—	$m = 0.8558\tau^{0.0179}$
1350	0.9774	0.9807	0.9949	0.9981	—	—	—	—	$m = 0.9000\tau^{0.0128}$

\* Initial size of sand grain 0.55 mm.

TABLE 2

Initial size of sand grain, mm	Share of SiO <sub>2</sub> that has reacted, %, for melting duration, * sec							Kinetic dependence $m = K \tau^n$
	300	600	900	1200	1800	3000	4800	
0.150	0.9766	0.9898	0.9933	0.9981	—	—	—	$m = 0.9274\tau^{0.0098}$
0.275	0.9180	0.9691	0.9833	0.9874	—	—	—	$m = 0.9011\tau^{0.0123}$
0.350	—	0.9577	—	0.9749	—	0.9936	0.9993	$m = 0.8800\tau^{0.0143}$
0.550	—	0.8998	—	0.9444	0.9715	0.9738	0.9797	$m = 0.8077\tau^{0.0232}$

\* Melting temperature 1250°C.

TABLE 3

Melting temperature, °C	Duration of complete melting of sodium silicate batches ( $M = 3.535$ ), sec, for initial size of sand grain, mm							
	0.150		0.275		0.350		0.550	
	Experimental data*	Estimated values	Experimental data*	Estimated values	Experimental data*	Estimated values	Experimental data*	Estimated values
1150	6840	7620	10,700	13,265	14,600	16,540	22,100	25,010
1200	4590	4800	7190	8365	9450	10,430	14,900	15,775
1250	3200	3090	5600	5380	6870	6705	10,600	10,140
1300	1980	2020	3140	3515	4300	4380	6550	6630
1350	1400	1340	2170	2335	2960	2915	4600	4405

\* Data from [1, 2].

$M = 3.535$ , with 22.6 wt.% Na<sub>2</sub>O and 77.4 wt.% SiO<sub>2</sub>. The mass content of SiO<sub>2</sub>, which at the preset melting temperature and melting duration remains without reacting in the glass melt, is found by using the chemical method of selective dissolution of glass in fluosilicic acid.

These kinetic dependences derived for the analyzed composition of sodium-silicate glass can be extended to other compositions using dimensionless notations:

$$m = \bar{\tau}^n; \quad \bar{\tau} = \frac{\tau}{\tau_c}, \quad (1)$$

where  $\bar{\tau}$  is dimensionless time or relative melting duration;  $\tau_c$  is the time of complete melting of quartz sand grains.

The appropriateness and validity of the technique used for generalization is corroborated experimentally [3]: the obtained dependences of sand dissolution rate on the glass composition represent a family of similar curves.

Let us estimate the effect of melting temperature and particle size (reaction surface area) on the power  $n$ :

$$n = 0.05 \exp(3\delta_0^2)(10^{-3}t)^{-7.5}, \quad (2)$$

where  $\delta_0$  is the initial grain size in the batch, mm;  $t$  is the melting temperature, °C.

For a quantitative estimate of diffusion processes based on the generalized kinetic depen-

dence, one should know  $\tau_c$ , i.e., the duration of complete dissolution of sand grains under a preset glass-melting regime.

We propose our own calculation formula (sec) based on the data in [1, 2, 4] for sodium silicate batches in a melting temperature interval of 1150 – 1600°C:

$$\tau_c = 6355(10^{-3}t)^{-10.83} \delta_0^{0.915} M^{2.717}, \quad (3)$$

where  $M$  is the silica modulus of the batch.

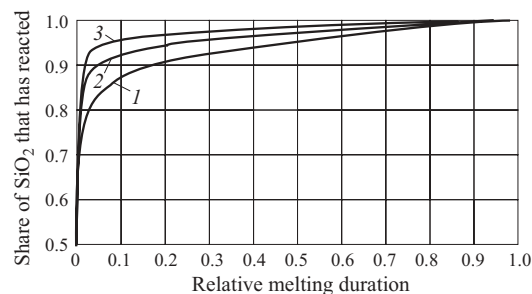
According to the above formula,  $\tau_c \sim \delta_0^{0.915}$ . A certain disagreement with the known relationship  $\tau_c \sim \delta^3/\delta^2 \sim \delta$  apparently reflects the deviation of the shape of real sand particles from the spherical shape.

Tables 3 and 4 correlate values  $\tau_c$  found experimentally and those calculated based on formula (3).

TABLE 4

Melting temperature, °C	Duration of complete melting of sodium silicate batches (initial size of sand grain 0.417 mm), sec, for silicate modulus					
	2.6		3.0		3.5	
	Experimental data*	Estimated values	Experimental data*	Estimated values	Experimental data*	Estimated values
1450	740	685	1140	1010	1660	1535
1500	525	475	890	700	1230	1065
1550	330	330	510	490	700	745
1600	190	235	300	345	435	530

\* Data from [4].



**Fig. 1.** Kinetic curves of dissolution of quartz sand grains with initial size 0.55 mm in melting of sodium silicate batch ( $M = 3.535$ ) at temperatures 1100°C (1), 1200°C (2), and 1300°C (3).

According to formula (3), the expected decrease in the melting duration of industrial sodium silicates with  $M = 2.6 - 3.6$  in the temperature interval of 1200 – 1500°C will be equal to 8.5 – 7.0% for each 10°C temperature increase and will be 13 – 14% for  $\text{Na}_2\text{O}$  content in glass increasing by each 1 wt.%. This means, in particular, that when a glass-melting furnace producing impure sodium disilicate with  $M = 2.8$  is converted to production of high-modulus sodium disilicate ( $M = 3.6$ ), the output of the furnace is expected to decrease by at least 40%. The output of the furnace can be maintained at the same level by raising the melting temperatures by 60 – 80°C.

The kinetic curves of  $\text{SiO}_2$  dissolution are shown in Fig. 1. One can distinguish segments corresponding to the stages of silicate and glass formation. At the silicate-formation stage the batch components enter in a chemical reaction

and form a silicate melt close to the initial batch composition. In this period the rate of the heterogeneous process of silica dissolution depends on the rate of the chemical reaction on the surface of  $\text{SiO}_2$  particles. With  $\bar{\tau} = 0.1$ , 90 – 95% of initial  $\text{SiO}_2$  becomes chemically bonded.

While boundary layers keep forming around the sand grains, the diffusion processes begin to have a more perceptible effect on dissolution, and the rate of dissolution decelerates. At the stage of glass formation the rate of dissolution stabilizes and depends only on diffusion mass exchange.

The use of generalized dependence (1) and formulas (2), (3) proposed by us makes it possible to reliably describe the kinetics of the diffusion process of glass melting in the  $\text{Na}_2\text{O} - \text{SiO}_2$  system, including industrial regimes of melting impure sodium disilicate.

## REFERENCES

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